



Reduction of Eu^{3+} to Eu^{2+} in Al-Codoped Silica Glasses Fabricated by the Sol-Gel Technique and CO_2 -Laser Processing

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Abstract. The spectroscopic properties of europium in aluminium codoped silica glasses produced by the sol-gel technique have been studied with respect to the dopant concentrations and the thermal processing applied to the samples. After thermal annealing at temperatures up to 950°C the bright red fluorescence around 613 nm characteristic for the trivalent europium ions (Eu^{3+}) has been observed. The lifetime was measured to be 0.1–2.4 ms depending on dopant concentrations and thermal treatment. Subsequent CO_2 -laser processing in air (short time remelting) gave rise to a bright blue fluorescence consisting of two broad bands, lying around 450 and 490 nm, with their peak position depending on the ratio between the aluminium and europium concentrations. The fluorescence lifetimes were found to be shorter than 1 μs . This blue fluorescence is attributed to the divalent europium ion (Eu^{2+}), leading to the conclusion that the CO_2 -laser processing of europium doped alumina-silica glasses resulted in the reduction of the trivalent to the divalent europium ion. Laser processing could therefore be a valid alternative to conventional thermal annealing for the generation of Eu^{2+} in alumina-silica glasses.

Keywords: sol-gel, trivalent europium, divalent europium, alumina-silica glasses, CO_2 -laser

1. Introduction

Rare earth ions or lanthanides in a glassy or crystalline host matrix are well known fluorescing materials and have therefore a wide range of applications from active materials for solid-state lasers and amplifiers to electro-optic devices and sensors. Europium is of particular interest for novel applications as trivalent ion with its luminescence in the orange-red as well as in its divalent configuration with a broad luminescence band from UV to blue-green [1, 2].

Trivalent europium is mainly used for remote high temperature sensing applications [3, 4], while crystals or ceramics doped with divalent europium ions find applications as blue emitting phosphors for plasma display panels and x -ray storage [5, 6]. Both forms of europium have been investigated in the past [e.g. 1, 2, 7] and even the transition from the trivalent to the diva-

lent ion at elevated temperatures and under a hydrogen atmosphere has been reported [8, 9], but to our knowledge this reduction has not yet been observed during laser induced short time melting under ambient conditions.

We investigated the spectroscopic properties, such as fluorescence spectra and lifetime, of europium and, in some cases, aluminium doped sol-gel derived silica with respect to the thermal treatment applied to the samples and their dopant concentrations. In this paper we report the reduction of Eu^{3+} to Eu^{2+} in alumina-silica glasses during thermal processing with a CO_2 -laser.

Laser processing could therefore offer a fast alternative to high temperature annealing under hydrogen atmosphere having the additional benefit of low sample contamination.

2. Experimental

Glasses or glass-like silica samples were produced from a solution of tetraethoxysilane (TEOS) and

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additives by the sol-gel method, which is described in detail elsewhere [10]. Dotation of the samples was achieved by adding europium nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) to this solution. Precursor solutions with europium ion concentrations relative to silica atoms from 0.1 to 10% were prepared. By assuming a final density of the samples equal to that of quartz glass, the europium concentration lies in the range of $2.2 \cdot 10^{19}$ to $2.2 \cdot 10^{21} \text{ cm}^{-3}$. Aluminium codoped samples were produced by adding an equal amount (0.1 to 10 at%) of aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) or ten times more aluminium (10% for a 1% europium doped sample) to the initial solution. The relative uncertainty of all concentrations is calculated to be approximately 10%. In the following, the samples are identified by their initial europium and, where applicable, aluminium concentration in atomic percent relative to Si.

Gelling of the solution and evaporation of solvents occurred at room temperature within several weeks, leading to monolithic samples of a size of several mm^3 . Drying at moderate temperatures up to 250°C lead to a further densification of the samples and evaporation of solvents.

The resulting samples were first examined without further thermal treatment. Subsequently the samples were annealed for several hours around 500 and 950°C in a conventional oven or laser processed (melted) using a CO_2 -laser. All thermal treatment was carried out under ambient air.

The fluorescence spectra of the red emitting samples were measured with a fluorimeter, while the spectra of the blue emitting samples were recorded with an Ocean Optics USB Spectrometer using a continuously emitting UV lamp (peak wavelength 370 nm) for excitation.

The fluorescence lifetimes were measured using a flashlamp (pulse length $\sim 10 \mu\text{s}$, peak wavelength 370 nm) for excitation and a photomultiplier with a monochromator and a suitable interference filter for detection of the emission.

3. Results

After drying at temperatures up to 250°C the europium and europium-aluminium doped silica samples revealed the bright red fluorescence characteristic for the trivalent europium ion (Eu^{3+}). Figure 1 shows the fluorescence spectrum recorded for a 10 at% europium doped silica sample. A series of sharp lines with FWHM $\sim 10 \text{ nm}$, the main line lying at 613 nm ,

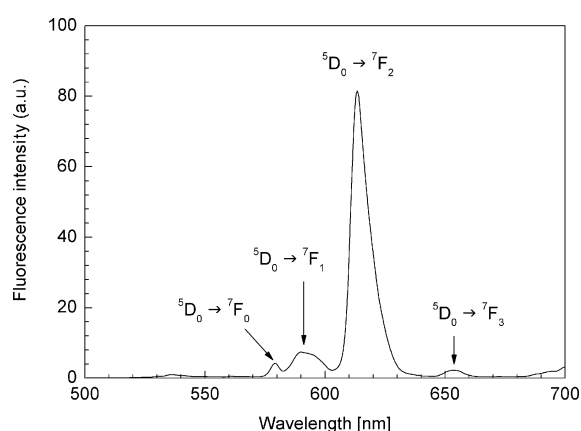


Figure 1. Fluorescence spectrum of 10 at% Eu^{3+} doped sol-gel derived silica.

was observed. Annealing at higher temperatures of 500 or 950°C resulted in an unchanged fluorescence spectrum.

The fluorescence lifetimes measured for the main emission line at 613 nm ranged from 0.13 – 2.40 ms , depending on the thermal treatment applied to the samples and their europium and, where applicable, aluminium concentration. The fluorescence lifetimes of silica samples doped with 1 at% europium are presented in Table 1. It was found that the fluorescence lifetimes of europium in the aluminium modified silica host material are slightly shorter than the ones in the

Table 1. Fluorescence lifetimes (at 613 nm) for 1 at% europium doped silica samples depending on the aluminium concentration and the annealing temperature.

Al-concentration (at%)	Annealing temperature ($^\circ\text{C}$)	Fluorescence lifetime (ms)
0	250	0.17
0	500	0.43
0	950	2.40
0	CO_2 -laser	— ^a
1	250	0.13
1	500	0.29
1	950	1.01
1	CO_2 -laser	— ^b
10	250	0.13
10	500	0.33
10	950	1.54
10	CO_2 -laser	— ^b

^aNo fluorescence observed.

^bBlue fluorescence observed.

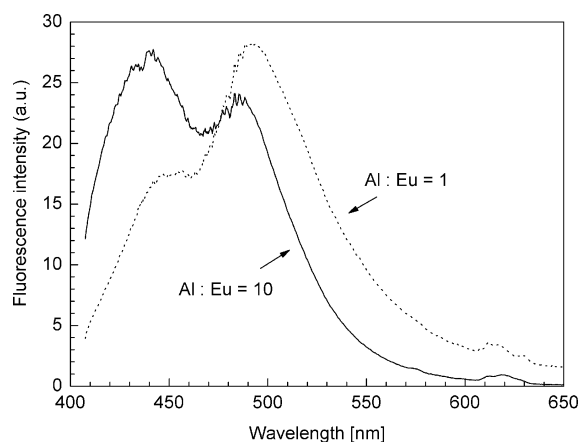


Figure 2. Fluorescence spectra of Eu^{2+} in aluminium codoped silica after CO_2 -laser processing and for different aluminium concentrations.

corresponding pure silica and that the lifetimes generally increased with increasing annealing temperature.

CO_2 -laser processing in air of the samples containing europium as well as aluminium gave rise to a bright blue fluorescence which is attributed to the divalent europium ion (Eu^{2+}) and comprises two broad bands (FWHM ~ 100 nm) spaced by about 40 nm. It was found that their peak wavelengths depend on the sample composition. For samples doped with an equal amount of europium and aluminium ($\text{Al:Eu} = 1$) the peaks lie at 457 ± 4 and 497 ± 3 nm, the latter being the stronger peak, while for samples containing more aluminium than europium ($\text{Al:Eu} = 10$) the peaks are slightly shifted to shorter wavelengths lying at 444 ± 3 and 487 ± 2 nm and the former being the stronger peak. Furthermore all samples showed a small red fluorescence around 613 nm arising from a fraction of trivalent europium ions still present in the samples. Figure 2 shows the fluorescence spectra for two samples having the same europium concentration but different aluminium concentrations. The fluorescence lifetimes could not be exactly determined, but were found to be shorter than $1 \mu\text{s}$ for all samples.

CO_2 -laser processing of the europium doped silica samples without aluminium did not lead to any observable blue fluorescence.

4. Discussion

A typical fluorescence spectrum of the europium and, where applicable, aluminium doped samples annealed

at temperatures up to 950°C is shown in Fig. 1 and reveals a series of sharp lines with FWHM ~ 10 nm which is characteristic for the transition from the first excited state to the ground state of the 4f-electron in trivalent europium. We identified four separate lines at 578, 594, 613 and 653 nm associated with the transitions from the $^5\text{D}_0$ level to the $^7\text{F}_0$, $^7\text{F}_1$, $^7\text{F}_2$ and $^7\text{F}_3$ level, respectively. These values are in good agreement with literature [1, 7] and we therefore conclude that the europium is incorporated in the silica samples annealed at temperatures up to 950°C in its trivalent form disregarding a potential aluminium codotation.

The observation of an increase in fluorescence lifetime of one order of magnitude with increased annealing temperature, as shown in Table 1, is explained by a reduced probability of concurring non-radiative decays associated with high-energy phonons present in the sol-gel derived host material. We have shown earlier [11], that a significant reduction of these phonons associated with OH-groups originating from solvents or not fully polymerised host material occurs during annealing at elevated temperatures and that this leads to a considerably prolonged fluorescence lifetime.

Similar results were found for samples doped with 0.1 and 10 at% europium, respectively, and for aluminium codoped samples, although the increase in lifetime was less pronounced for the samples containing 10 at% europium, presumably due to concentration quenching.

After CO_2 -laser processing, the europium and aluminium codoped silica samples revealed a bright blue fluorescence, as shown in Fig. 2, with fluorescence lifetimes shorter than $1 \mu\text{s}$.

We conclude, that this blue fluorescence is attributed to divalent europium ions (Eu^{2+}) present in the host material after laser processing, since high purity chemicals ($>99\%$) have been used to synthesise the samples and no other rare earth ions were present during the sol-gel process and the laser treatment. Furthermore blue fluorescence from Eu^{2+} is not unusual given that the ion readily emits light in a wide range from near UV to green, depending on the surrounding host material [2]. In amorphous host materials and glass ceramics two peak emissions have been observed [9, 12] and the lifetimes given in literature [13] correspond with our measured upper limit of $1 \mu\text{s}$. It is also known, that the reduction of Eu^{3+} to Eu^{2+} occurs at elevated temperatures of about 1100°C in hydrogen atmosphere and can be reversed by applying an oxygen atmosphere [8, 9].

The fluorescence spectra of all investigated samples doped with europium and aluminium were comparable after CO₂-laser processing, all having two lines but with slightly different peak wavelengths and intensity ratio of the two peaks. The evidence points in the direction of these differences being a function of the aluminium and europium concentrations. At low aluminium to europium ratios (Al:Eu = 1) the emission at longer wavelength (494 nm) is stronger, while at higher ratios (Al:Eu = 10) the spectrum is shifted to shorter wavelengths and dominated by the line at 442 nm. Since the ground state for divalent europium consists of a single level (⁸S_{7/2}), we presume, that the surrounding host material affects the position of the excited 5d¹-level. The evidence suggests that two different sites for the incorporation of the Eu²⁺ ion are present in the laser processed materials, even though they are amorphous, but further experiments will be carried out to corroborate this assumption.

Furthermore we discovered that during CO₂-laser processing in air the reduction of Eu³⁺ to Eu²⁺ is not complete. A small fraction of the ions remains in the trivalent state and their weak red fluorescence is still found in the fluorescence spectra. Further experiments are planned to clarify the conditions under which incomplete reduction occurs.

Our results show that CO₂-laser processing under ambient conditions allows to produce divalent europium in alumina-silica glasses and could therefore be a fast alternative to high temperature annealing in a hydrogen atmosphere, having the additional benefit of low sample contamination.

5. Conclusion

We investigated the spectroscopic properties of europium in aluminium codoped sol-gel derived silica in view of the dopant concentrations and thermal treatment. We found that CO₂-laser processing of the samples gave rise to a bright blue fluorescence that consists of two broad lines with lifetimes shorter than 1 μs, and is attributed to divalent europium ions present in

the host material. The two emission lines are probably associated with two different sites occupied by the europium ions in the host material and their peak wavelengths are related to the aluminium and europium concentration. We therefore conclude that a reduction of Eu³⁺ to Eu²⁺ occurs in aluminium doped silica during the CO₂-laser treatment in air. Laser processing turned out to be a fast and low contamination alternative to high temperature annealing under hydrogen atmosphere.

Acknowledgments

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